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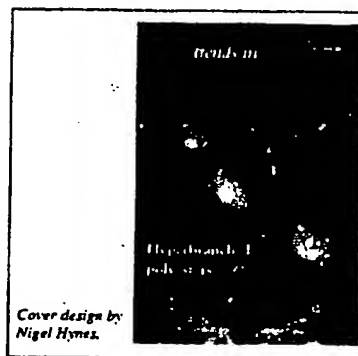
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- 25 Kawagoe, M. and Nunomoto, S. (1991) *Polymer* 32, 3130
- 26 Eccott, A.R., Arnold, J.C. and Isaac, D.H. (1994) *Mater. Res. Soc. Symp. Proc.* 22, 205 [High Performance Polymers and Polymer Matrix Composites]
- 27 Arnold, J.C., Li, J. and Isaac, D.H. (1996) *J. Mater. Proc. Tech.* 56, 126
- 28 Arnold, J.C. (1994) *Polym. Eng. Sci.* 34, 665
- 29 Wright, D.C. and Cotham, K.V. (1983) *Polym. Eng. Sci.* 23, 135
- 30 Wright, D.C. (1978) *Br. Polym. J.* 10, 60
- 31 Kawagoe, M. and Kitigawa, M. (1990) *J. Mater. Sci.* 25, 1043
- 32 Menges, G. and Schmidt, H. (1967) *Kunststoffe* 57, 885
- 33 Menges, G. and Riess, R. (1974) *Plast. Polym.* 42, 119
- 34 Brüller, O.S. (1978) *Polym. Eng. Sci.* 18, 42
- 35 Kawagoe, M. and Kitigawa, M. (1981) *J. Polym. Sci., Polym. Phys.* 19, 1423
- 36 Kawagoe, M. and Kitigawa, M. (1987) *J. Mater. Sci.* 22, 3000
- 37 Kawagoe, M. and Morita, M. (1994) *J. Mater. Sci.* 29, 6041
- 38 Kawagoe, M. and Kitigawa, M. (1988) *J. Mater. Sci.* 23, 3927

PE100 Resins for Pipe Applications:

Continuing the Development into the 21st Century

John Scheirs, Ludwig L. Böhm, Jesse C. Boot and Pat S. Leever ■

New tandem reactor polymerization technology is creating exciting developments in the polyolefin industry, such as polyethylene (PE) grades possessing a bimodal molecular weight distribution (MWD). These grades benefit from their bimodality by having the strength and stiffness of high-density PE, whilst retaining the high-stress-crack resistance and processability of unimodal medium-density grades. Such PE100 resins are ideally suited to the demanding application of pipes for gas and water distribution. To qualify for the PE100 rating, the polymer must withstand a minimum circumferential (hoop) stress of 10 MPa for 50 years at 20°C. Bimodal polyethylenes that fulfil this requirement without compromising other properties allow pipe industry standards to be met with lighter weight pipes or pipes with the same wall thickness as before but exhibiting significantly wider safety margins. This review will focus on the manufacture, structure, properties, characterization and future development of these new polymers.

Polyethylene (PE) pipes offer distinct advantages compared with other piping materials because they are lightweight, corrosion-free, exhibit very high ductility and allow all-welded construction. Furthermore, PE pipe up to diameters of 160 mm is flexible and can be coiled, thus

reducing installation costs and reducing the number of on-site welds required.

First- and second-generation PE pipes for water and gas distribution have minimum required strength (MRS) ratings for respective hoop stresses of 6.3 and 8 MPa, and are known as PE63 and PE80 respectively¹. The third-generation materials, which are known as PE100 resins, are those that conform to the MRS 10 rating. The rating is based on the ISO test method², which specifies that pipes manufactured from these materials should withstand a circumferential (hoop) stress of 10 MPa at 20°C for 50 years. PE100 resins are thus high-density polyethylene (HDPE) grades characterized by exceptionally high environmental stress-crack resistance, good resistance to rapid crack propagation (RCP) and very high creep resistance.

The first reports of PE100-type resins appeared in the late 1980s when Solvay released its new Eltex® TU B 120 series pipe grades³⁻⁵. Since then, other polyolefin manufacturers have actively engaged in research, in a race to develop these compounds. To date, very little literature has been published on how to design a PE100-type material because of its proprietary nature. However, it has been established that the key criterion is the requirement to concentrate all the short-chain branches in the high molecular weight (MW) fraction of the polymer chain length distribution. This can only be achieved by using a tandem or cascade reactor system, or by using a dual-site catalyst, to obtain the desired bimodal MWD.

PE100 resins provide important property advantages over the earlier PE63 and PE80 grades when used for gas-distribution pipelines (see Table 1), thus affording superior safety margins. There are currently four commercial suppliers of PE100 resins. Hoechst have recently introduced their Hostalen CRP 100 grades, which are an improved 'crack resistant' version of their earlier PE100

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Table 1. Key performance properties for commercial pipe resins

Property	PE80	PE100
Yield stress/MPa	20	24
Elongation/(%)	>600	>600
Elastic modulus/MPa	750	1200
MRS ^a (over 50 years at 20°C/MPa)	8	10
Onset temperature for RCP ^b /°C	0	-10 to -20

^aMRS, minimum required strength (long-term hoop stress).
^bRCP, rapid crack propagation.

grade (GM 5010 T2 E100). It is available in black or blue and has a nominal melt flow index (MFI) of 0.22 g per 10 min (5 kg load at 190°C) and densities of 0.958 and 0.949 g cm⁻³, respectively. BP have recently commercialized their version of PE100-type resins, denoted Rigidex PC4100F and PC3100F, which are black and blue, respectively, and have the same MFI and density characteristics as the Hoechst grades. Borealis now market two grades of PE100 (HE2490 and HE2494) previously commercialized by Neste. These are lower molecular weight (MW) versions of the Hoechst and BP grades above, and the black and blue grades have a nominal MFI of 0.40 g per 10 min (5 kg load at 190°C) and densities of 0.961 and 0.954 g cm⁻³, respectively. The Eltex TU B series of PE100 resins by Solvay is available in black, blue and yellow with nominal MFIs of 0.45, 0.48 and 0.48 g per 10 min and densities of 0.959, 0.954 and 0.952 g cm⁻³, respectively. These grades also differ in key properties such as slow crack-growth (SCG) resistance⁶ and RCP (Ref. 7). Such property data are given in product literature⁸⁻¹¹.

Manufacture

Bimodal PE resins are produced by tandem processes that use reactor combinations of loop, slurry and gas-phase by themselves or in combination with each other. The high MW component is generally made in the first reactor and then the partially formed polymer particles are transferred to the second reactor where the lower MW component is formed (Fig. 1a). A comonomer, such as butene or hexene, is added along with ethylene during the first stage of the process to incorporate a high level of branching preferentially in the high MW component of the polymer.

Borealis employ a hybrid reactor bimodal process based on a slurry-loop-reactor-gas-phase reactor configuration¹² (see Fig. 1b) in which supercritical propane has replaced isobutane as the diluent. The diluent serves as the polymerization medium and facilitates transfer and removal of the substantial heat of polymerization of ethylene. Slurry polymerization processes used by different HDPE manufacturers can be classified into three categories: (1) loop reactors with a light diluent such as isobutane, which is used by licensees of the Phillips process; (2) loop reactors with a heavy diluent such as hexane, which is used by Solvay; and (3) continuous stirred-tank reactors with a heavy diluent, used by Hoechst and several Japanese polyolefin companies¹³. The heavy-diluent,

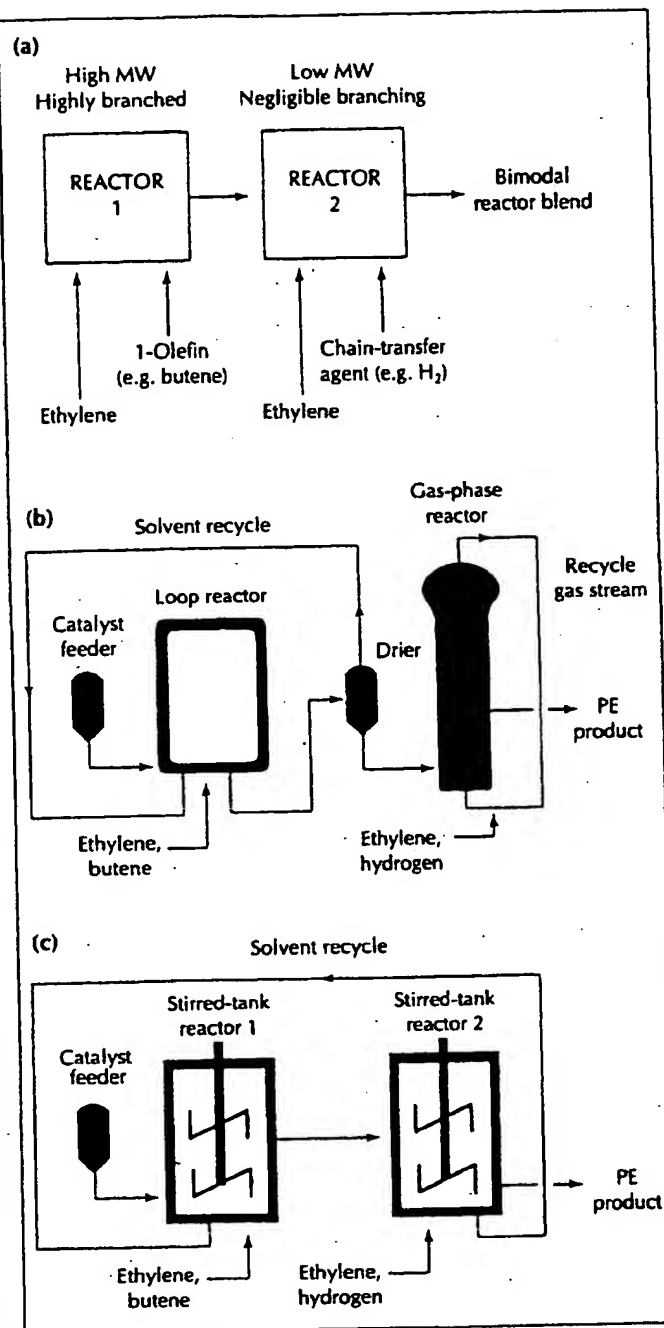


Fig. 1 (a) Idealized schematic of a tandem polymerization process to produce bimodal PE100, (b) hybrid slurry-loop-gas-phase configuration employed by Borealis and (c) cascade continuous stirred-tank slurry reactors employed by Hoechst.

continuous stirred-tank reactor series concept (also known as tandem slurry) is used by Hoechst to produce their PE100 resin by a 'cascade polymerization' process (Fig. 1c).

Cascade polymerization is a sophisticated process that employs third-generation catalysts (comprising titanium-based catalysts supported on silica together with

alkylaluminium cocatalysts) and involves transferring the reactor particles from one reactor to another to tailor the MWD. In this process, the resin is produced by carefully forming the high MW component then adding hydrogen gas to the ethylene stream, which acts as a chain-transfer agent and thus produces the low weight fraction, to give the nascent polymer particles that are composed of micrograins, as shown in Fig. 2. Such resin may be viewed as being a reactor 'blend' ¹⁴.

The art in producing PE100-type polymers is to tailor the polymerization of the low and high MW fractions, such that the former component achieves an MFI in excess of 500 g per 10 min (5 kg at 190°C) while the latter component has a very high average MW, above 8×10^5 g mol⁻¹, to establish an MFI in the range of 0.2 to 0.5 g per 10 min in the final polymer. The average MW, which is inversely proportional to MFI, is controlled by varying the hydrogen:ethylene ratio during polymerization.

To generate a very broad bimodal MWD it is necessary to have two fractions with fairly different average MW. The ratio of the viscosity-average MW of both fractions $M_{v2}:M_{v1}$ determines bimodality ¹⁵. This is best accomplished by a two-stage polymerization process with either continuous or discontinuous operation. It has been found that the ratio $M_{v2}:M_{v1}$ must be at least ten to obtain resins with two distinct peaks in the MWD ¹⁵. It is important to note that it is very difficult to achieve a truly homogeneous bimodal blend solely by mechanical blending of the two fractions. However, the polymer blend formed in the cascade technology also has to be well homogenized during the extrusion process using an intensive mixing device coupled to a plasticating extruder such as a continuous mixer (e.g. Farrell™18UM) ¹⁶.

Processing considerations

PE100 materials require no special processing conditions and can be processed in the same way as PE80 and earlier pipe grades. This is possible by virtue of their bimodal MWD as the inherent lubricating effect of the low MW component offsets the high melt viscosity of the high MW fraction. Pittman *et al.* ¹⁷ have investigated the heat-transfer coefficients for PE80 and PE100 pipes during

manufacture. The cooling process after extrusion is critical because it influences both the development of the microstructure and the residual stress in the pipe.

Molecular properties

Different grades of PE resins intended for a diversity of applications show variations not only in their average MW and density but also in their molecular architecture. For instance, injection-moulding grades typically have a low MW and a narrow MW distribution (i.e. low polydispersity) but, also, the chain branches are often in the low MW tail of the polymer. In fact, for most conventional unimodal HDPE copolymers, the degree of branching is highest in the low end of the MWD and is very low for most of the longest polymer molecules ¹⁸. On the other hand, PE100 pipe resins have a higher MW (since impact strength depends mainly on the number-average MW) but, more importantly, the branching is mainly in the high MW tail of the weight distribution (see Fig. 3), for enhanced fracture toughness and stress-crack resistance. Thus, in PE100 resins the superior performance over traditional HDPE is achieved by tight control of MW and advantageous placement of short-chain branching. It has been shown that the side branches become effective in enhancing toughness if they are placed on molecules with MW greater than 150 000 (N. Brown, pers. commun.).

The penalty for having a high MW component is decreased processability and an increased likelihood of extrusion defects such as melt fracture. Bimodal MWD polymers overcome this problem by 'having the best of both worlds', through the incorporation of a very low MW fraction as well, which aids processability by an inherent lubrication effect.

The low MW fraction, which is sparsely branched, is largely responsible for forming the crystalline phase in the solid state. The amorphous phase constitutes predominantly the high MW fraction within which resides a high concentration of tie molecules ^{19,20}. Tie molecules are those polymer chains that connect adjacent crystallites and thus act as load-bearing members. Thus, the density of polyethylene can be controlled by variation of the level of comonomer. At the same comonomer content the bimodal PE100 resins reach a higher degree of crystallinity, which causes further improvement in elastic modulus, stiffness and yield strength. Or viewed in another way, PE100 resins have a higher degree of comonomer incorporation for a given density (or crystallinity) compared with PE80 resins (Fig. 3c). This causes a considerable increase in the degree of entanglements of polymer chains, thus improving the mechanical properties.

Tie molecules contribute to SCG resistance by anchoring the fibrils that form at the crack tip during crazing, which precedes SCG. Maximum protection is offered by those tie molecules that possess short-chain branches, because these effectively hinder the pullout of the polymer chain from the crystallites. It is thus the long chains with the most comonomer incorporation that provide the highest fracture toughness ²⁰. Chain entanglement is higher for PE100 resins, so disentanglement at the crack tip, which is the governing factor where brittle failure is concerned, is far less pronounced with PE100 compared with PE80 and PE63 resins.

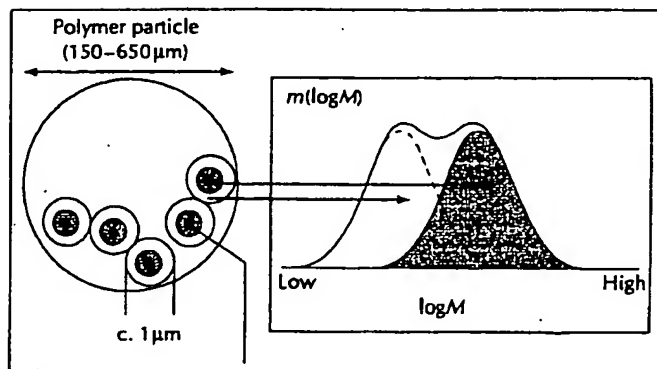


Fig. 2 Schematic of nascent PE100 polymer particles, which are composed of micrograins that are produced by polymerizing the highly branched, high molecular weight component in one reactor followed by production of the low weight fraction in a second reactor. M represents molecular weight and m is the mass fraction.

Analytical characterization

The best way to characterize PE100 materials is using polymer fractionation methods to deconvolute their bimodal architecture. In particular, fractionation methods allow determination of the comonomer composition (i.e. the comonomer content as a function of MW)^{21,22}, which, besides the MWD, is one of the most important molecular parameters for PE100 resins. The comonomer content of PE100 resins is generally 40% higher than that of a traditional PE resin of the same density. One of the most informative methods is temperature-rising elution fractionation (TREF) combined with analytical size exclusion chromatography (SEC)²³ and ¹³C-NMR, which yields information on the MW and branch content of each fraction, respectively.

Investigation on PE pipe materials can also be done by the Holtrup fractionation method²⁴ combined with IR analysis to determine the degree of short-chain branching of each fraction^{18,25}. This direct extraction method is a relatively simple method for determining the comonomer content as a function of MW. A sophisticated refinement of this method is to analyse the fractions produced by the Holtrup fractionation using SEC and ¹³C-NMR.

Fractionation methods, however, are laborious and time-consuming. Recognition of the critical influence of comonomer distribution on PE100 properties has prompted the search for an alternative characterization method, suitable for routine batch monitoring. A technique based on differential scanning calorimetry (DSC) known as stepwise isothermal segregation (SIS) has been recently developed and calibrated against fractionation data^{26,27}. Before testing under the constant heating ramp conventionally used in DSC, each sample is melted and cooled through a sequence of isothermal steps. Each step stabilizes a crystalline fraction characterizing a region of the comonomer distribution spectrum, so that this spectrum emerges in a fine structure of heat input peaks on subsequent reheating. The DSC peak structure for PE100 is particularly complex, and has revealed subtle batch-to-batch variations.

Mechanical properties

PE100 materials have chains that are branched and entangled but not crosslinked, and therefore they have time-dependent (viscous) properties qualitatively similar to those of PE80 and earlier generation polyethylenes. Polyethylene normally behaves in a ductile manner but as stress levels reduce and service lives increase, SCG at defects (e.g. flaws and notches) can result in brittle failure²⁸. Slow crack growth, as its name suggests, is a very slow process with crack propagation speeds of the order of $1 \times 10^{-5} \text{ m s}^{-1}$.

On the other hand, a completely different mode of brittle failure, known as rapid crack propagation (RCP), can be observed when an impact-initiated crack propagates at speeds up to 300 m s^{-1} along the entire length of the pipe²⁹. Thus, the pattern of development of successive generations of PE pipe materials has been to reduce progressively the risk of brittle behaviour so that the potential benefits of the highly ductile regime can be more fully exploited. The current generation of PE80 resins, for example, have excellent SCG resistance but have less than optimum resistance to RCP, particularly

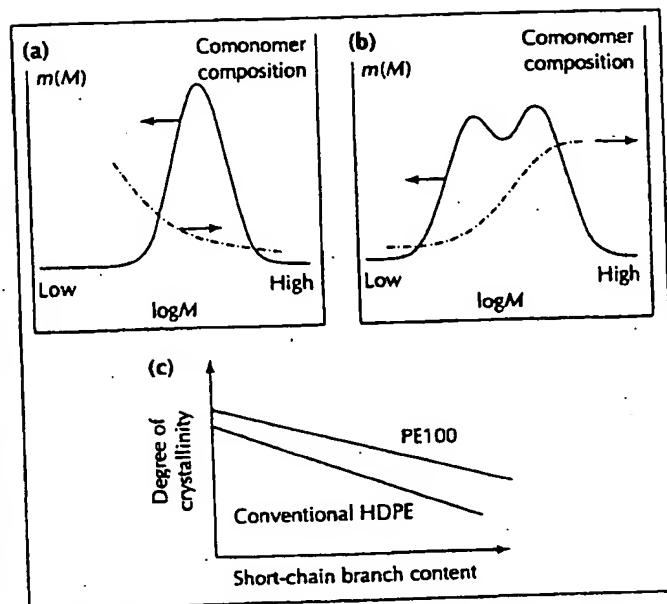


Fig. 3 Relationship between the molecular weight distribution ($m(M)$; —) and comonomer content (---) as a function of molecular weight for (a) conventional unimodal PE resin and (b) bimodal PE100 material. (c) Relationship between crystallinity (or density) and short-chain branch content for conventional HDPE (i.e. PE63 or PE80) and PE100 resins.

at larger diameters³⁰. Furthermore, earlier attempts to improve RCP performance caused a concomitant reduction in SCG resistance.

Ductile behaviour

Figure 4 shows standard tensile test results³⁰ for both PE80 and PE100. The short-term modulus is normally quoted³¹ as the initial tangent to the tensile curve. Figure 4 yields short-term moduli for PE80 and PE100 of 750 and 1200 MPa, respectively.

It should be noted that these properties were obtained using samples cut from pipe; polymer manufacturers commonly quote fundamental properties based on samples cut from sheet, which have been annealed and thus give higher values.

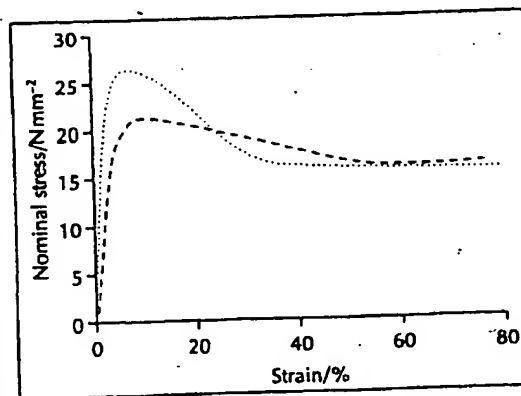


Fig. 4 Typical tensile test results for PE80 (---) and PE100 (.....) resins (crosshead speed, 100 mm min^{-1} ; room temperature).

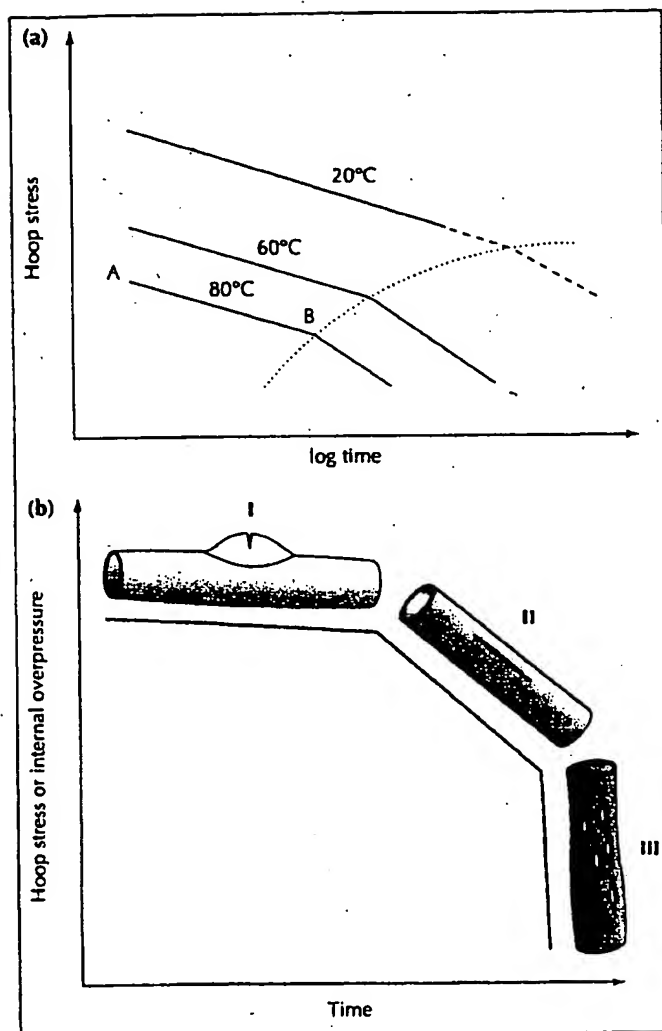


Fig. 5 (a) Qualitative illustration of the results of standard pressure testing on a typical polyethylene pipe over a range of temperatures. The knee at B is accompanied by a gradual change in failure mode from ductile to increasingly brittle behaviour owing to slow crack growth (—, actual data; ----, projected data; ·····, extrapolation of the time of the 'knee' to lower temperatures). (b) Schematic representation of the creep rupture failure modes encountered during different stages of pressure testing of HDPE pipe: I, ductile failure; II, knee; and III, brittle failure. (Courtesy of M. Ifwarson, Studsvik Material AB, Sweden.)

The viscous nature of these materials can most easily be studied by performing a tensile test at constant load and observing the consequent increase in deformation with time (creep). If a stress less than the maximum tensile stress of the polymer is applied for a short period (hours or days), the behaviour of the polymer is essentially viscoelastic, and up to 95% of the deformation is gradually recovered upon removal of the load. Conversely, if the load is removed after a significant period of creep deformation (over weeks or months) only about 30% recoverable deformation is obtained (Z.W. Guan, PhD thesis, University of Bradford, 1993). It is also important to note that the ductile properties of PE are not only resin, process and strain-rate dependent but are also

a significant function of temperature, with short- and long-term moduli reducing, typically, by 300% and 50%, respectively, as ambient temperature rises from 20 to 40°C.

It should not be assumed that creep under loading is necessarily destructive. When PE pipes are subject to service loading, long-term deformations are less than 5%, whilst under restrained conditions, creep results in a highly beneficial stress redistribution with time. In a stress analysis simulating the creep behaviour of a 6 mm thick PE100 lining subject to 3.2 MPa internal pressure whilst spanning a 60 mm diameter void in a host pipe, it was found that, upon initial application of load, stress levels in excess of 16 MPa at the midspan were measured and these are of a magnitude sufficient to cause rupture in an unrestrained pipe. However, after one month, creep has adjusted the deformations so as to reduce these stresses to below 11 MPa.

Stress concentrations caused by point loads, inconsistent backfill, variable ground support and so on are all mostly dissipated by the effects of creep. These characteristics of PE pipe materials are a major reason why there are no reported problems in PE pipelines due to longitudinal or temperature effects, and no reported problems of any kind directly attributable to material behaviour (i.e. not installation related) in PE80 and PE100 pipes.

Slow crack growth

To be able to take full advantage of the above characteristics, it is necessary to ensure that any failure will in fact be ductile. Figure 5a illustrates qualitatively the results of a series of pressure tests undertaken on a typical PE material over a range of temperatures. As pressure decreases from the short-term burst value, creep life increases along a line such as AB; beyond B creep life only increases in a significantly smaller proportion³². The 'knee' at B is accompanied by a gradual change in failure mode from ductile to increasingly brittle behaviour (owing to SCG). This shifting behaviour is observed because resistance to fracture decreases more rapidly with time than resistance to yielding. To ensure the maintenance of specified safety factors, great care is required when extrapolating relatively short-term results (usually obtained in less than 1 year) to yield the MRS at 50 years. This is achieved by pressure testing to produce results as indicated in Fig. 5a and interpreting these according to the standard extrapolation method (SEM)². The basic principle of the SEM is that the time to the 'knee' reduces with increasing temperature; thus the possibility of ductile-brittle transition at 20°C can be predicted from results obtained at higher temperatures, as indicated by the dotted line in Fig. 5a. Figure 5b shows schematically the types of pipe failures that occur as a function of time. As the knee is approached the failure mode shifts from ductile (ballooning behaviour) to brittle, whilst beyond the knee brittle failures predominate.

First-generation PEs yield a knee at less than 50 years, and there have been cases of reported brittle failures with these materials²⁸. For PE80 materials, a knee can be implied at a time significantly in excess of 50 years⁹. In the case of PE100, creep pressure tests at 80°C for periods in excess of 10⁴ hours have failed to reveal any evidence of a 'knee'¹¹. However, SEM testing is undertaken using undamaged pipe, whilst standard specifications

permit a notch (10% of the wall thickness) in the pipe wall due to pipe handling and installation. To evaluate performance under these conditions several other tests have been devised³³⁻³⁵. In particular, extensive data³⁶ from the notched pipe test suggests that some PE100 materials are now not as resistant to SCG as PE80. This potential reclassification of these materials at different flaw sizes is the subject of ongoing research. However, it must be emphasized that one of the main problems in this respect is the great difficulty encountered in producing SCG in either PE80 or PE100 at anything approximating representative service conditions; both materials have SCG resistance well in excess of the required specifications³³.

Rapid crack propagation

PE pipes have been linked in the past to the phenomenon of RCP (Ref. 7). This is a process whereby an impact collision at one end of a pipe propagates rapidly along the entire length of the pipe. Essentially, the pipe 'unzips' in a distinct wavy manner at high speed. Pipe manufacturers conscious of this problem have lowered the maximum specified pressure for large diameter PE pipes because of the higher purported susceptibility of some grades to RCP. Whilst all PE100 resins have now been characterized with respect to RCP, it is not well understood what molecular and/or morphological parameters affect RCP.

Full-scale RCP tests have for many years been carried out on long, air-pressurized, buried PE pipe specimens, but this 'gold standard' method^{29,37} lacks practicality for routine testing. For quality control, and for research on new resins, the S4 (small-scale steady-state) test⁷ is used. This involves measuring the arrest length (i.e. distance travelled by the crack before it stops) of a fast crack, initiated by impact, in each of a series of tests at progressively increasing pressures. The arrest length remains about one pipe diameter until, above a well-defined critical pressure, it jumps to the entire specimen length. Because scaling down the test necessarily involves removing the surrounding sand or gravel bed and eliminating large-scale flow within the pressurizing medium, this critical pressure is much lower than the full-scale value. For a given PE resin at a given test temperature the higher the critical pressure the better the rapid-crack resistance of the resin.

At a sufficiently low temperature, all PEs seem to show similar critical pressures, as shown in Fig. 6. At 0°C (the lower design temperature usually assumed for both gas and water pipe) PE80 resins are very effectively distinguished by their S4 critical pressures. However, a bimodal PE usually does not yield a critical pressure above -10°C, and PE100 resins are therefore better characterized by the transition temperature above which the critical pressure abruptly increases³⁸. Thus, for PE100 pipes to undergo RCP a temperature much lower than that normally encountered for a buried gas pipe (and impossible for a water pipe) is necessary, making RCP extremely unlikely to occur in practice with PE100 generation pipes.

Although enhanced RCP resistance is a key feature of PE100, it must be exploited with care. Tests at temperatures just above the RCP transition show that increasing wall thickness has a similar effect to a further reduction in temperature³⁸. The abruptness of the transition temperature, its proximity to 0°C, the depth of any sharp

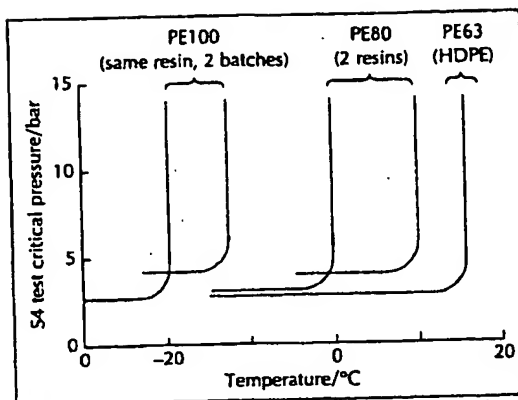


Fig. 6 Critical pressure for RCP as a function of temperature for PE63, PE80 and PE100 pipes in the small-scale steady-state (S4) test (test performed on pipes of diameter 90 mm and thickness 8.1 mm). Note: PE100 only undergoes RCP at very low temperatures (i.e. -10 to -20°C), which are not encountered in service, thus PE100 pipes can effectively be regarded as resistant to RCP.

scores along the pipe bore³⁹ and the tendency for batch-to-batch variation all demand close quality-control monitoring. British Gas still tests every PE100 batch for resistance to RCP at three times the maximum system pressure. While ductile behaviour suggests that the greater strength of PE100 resins can be exploited either by making pipes with thinner walls or by raising the operating pressure, RCP performance provides strong reasons to opt for the former.

The RCP behaviour of PE100 resins is complex, and not all details are yet understood. PE100 has both a higher dynamic modulus and a higher yield stress than PE80 (N.N. Diah, PhD thesis, University of London, 1993); in these respects it resembles PE80 at a lower temperature. Methods have been devised to measure resistance to fast, steady crack propagation (rather than to impact crack initiation) in compression-moulded plaques (e.g. the Izod impact test). Unlike S4 tests, these do sustain RCP in PE100 at 0°C but they show its resistance to be at least 50% higher than that of PE80 (Ref. 40). It has been suggested that RCP takes place by a process of adiabatic melting, at the scale of an extended chain length, beneath the roots of craze-tip fibrils⁴¹. Thus, PE100 resin owes its higher crack resistance mainly to its higher weight-average MW. PE100 pipe, however, seems to mobilize additional mechanisms to resist RCP, and some of these are undoubtedly sensitive to processing conditions. The increased speed of stress waves in PE100 may also increase the decompression wave speed down the pipe, thereby reducing the crack driving force.

Research by pipe manufacturers to address RCP has been aimed at producing pipes with a ratio of crack length to pipe diameter of approximately one, even at internal pressures of 2.0 MPa (Ref. 15). Resistance to RCP is a critical parameter to consider when designing and manufacturing pipes from PE100 resins, particularly pipes used for gas distribution, because a RCP failure would have obvious disastrous consequences. RCP can ensue when the pipe is subjected to high impact forces but it can also originate from other sources like a defective butt fusion weld. A new PE100 resin⁴ recently developed by Hoechst has demonstrated outstanding resistance to RCP.

Impact resistance

High-speed impact is used to initiate RCP in pipe tests but has not been responsible for any of the few documented RCP service failures. Conventional notched impact tests (e.g. Charpy or Izod) on PE resins do produce a fracture surface that in some respects resembles that from RCP but their use has been eclipsed by that of RCP tests on whole pipe sections. The relationship between impact crack initiation resistance and RCP resistance has never been clear.

Nevertheless, there are correlations between impact test results and RCP performance, and these have been used to guide PE100 resin development. Standard impact test results are expressed in terms of absorbed energy and, for amorphous polymers, instrumented impact tests on sharply notched specimens can yield a definitive fracture toughness. Tough polymers like PE100 are more complex: as impact speed increases, impact fracture resistance falls steadily⁴² so that no definitive values emerge. Thus, again, for PE100, the transition temperature rather than resistance in itself has become the focus of attention. Increasing the impact test temperature precipitates a brittle-to-tough transition similar to that seen in pipes. The use of impact transition temperature tests to guide small-batch production of experimental resins has produced some resins with brittle-ductile failure transition temperatures lower than -30°C.

Welding behaviour

PE pipes are joined either by heating the butt end of the pipe with a plate resistance heater, then mating the hot butt ends together to form a weld, or by an electrofusion technique employing resistively heated fittings. PE100 materials require different butt fusion conditions to PE80 grades, such as lower pressure during fusion. Furthermore, in the application of PE100 materials for thick-walled (up to 60 mm) water pipes it is necessary to use a dual pressure welding process to give weld tensile test ductility equivalent to that for the smaller sizes of pipes made from PE80 material⁴³. The effect of pipe wall thickness and welding parameters on the joint quality of butt fusion welded PE100 pipes has recently been investigated using notched Charpy impact and tensile tests⁴³.

Future trends

PE100 pipes have been getting progressively 'bigger' both in diameter and in market volume. There are now applications for gas distribution that use PE pipes of 800 mm in diameter, and this dimension could increase in the future. The new Hostalen CRP 100 grade offers the chance to produce pipes with diameters up to 2.6 m and wall thicknesses of 50 mm (Ref. 44). As the diameter increases so too does the demanding nature of the application. This underlines the need for resins with improved resistance to RCP. In this respect PE100 has enormous growth potential given the need for infrastructural developments of gas and water distribution networks worldwide. The forecast growth for PE100 materials in Europe is about 25% per year, and this is expected to progressively rise as the expected increases in the availability of fittings and larger diameter pipes are realized. A big market opportunity for PE100 also lies in water distribution. PE100 can successfully challenge ductile iron pipes up to diameters of 315 mm (Ref. 44).

The west European HDPE pipe grade market is anticipated to grow from 550 000 tonnes per year in 1994 to 800 000 tonnes per year by 2005, with PE100 accounting for 100 000 tonnes per year by then⁴⁵. Furthermore, major PE producers are adding PE100-type resins to their product range. BP are on the verge of commercialization of a Rigidex PE100 grade. BASF have recently announced that their researchers are working on a grade of Lupolen 3822 D aimed at the PE100 classification⁴⁶.

As most PE producers have now mastered cascade (tandem) reactor technology, what were novel configurations such as loop-loop, gas-phase-gas-phase and various combinations of these are now becoming standard processes¹². Furthermore, polymerization advances are enabling higher comonomer incorporation in the amorphous portion of the polymer, which considerably increases the entanglement of the molecular chains, and, therefore, further gains in fracture toughness are possible. In fact, PE112 and PE125 are already looming on the horizon with current innovations in polymerization technology promising to shorten the 'generation gap' considerably.

Together with new catalyst technologies and the use of hitherto unexploited strength enhancement techniques such as molecular orientation, the future of PE100 (and higher classification resins) is bright as it has the potential to displace medium-density PE and ductile steel pipes, thereby making it the keystone of gas-distribution systems worldwide.

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References

- ISO (1995) *Thermoplastic materials for pipes and fittings for pressure applications - Classification and designation: Overall service (design) coefficient*: ISO/DIS 12162.2, International Organization for Standardization, Geneva, Switzerland
- ISO (1994) *Thermoplastic pipes for the transport of fluids - Methods of extrapolation of hydrostatic stress rupture data to determine the long-term hydrostatic strength of thermoplastic pipe materials*: ISO/TR 9080, International Organization for Standardization, Geneva, Switzerland
- Anon. (1989) *Mod. Plast. Int.* October, p. 35
- Dewitt, R. (1992) *Proc. Plastic Pipes VIII, Eindhoven, The Netherlands*, pp. C2/2-1-C2/2-7 [available from: Plastics and Rubber Institute, 11 Hobart Place, London, UK SW1W 0HL]
- Yernaux, J.-M. (1992) *Polymer Developments for Pipe Systems*, presented at Polyethylene - the 1990's and Beyond, London, 19-20 May 1992 [available from: Plastics and Rubber Institute, 11 Hobart Place, London, UK SW1W 0HL]
- Huang, Y.L. and Brown, N. (1991) *J. Polym. Sci., Polym. Phys.* 29, 129
- ISO (1995) *Thermoplastic pipes for the conveyance of fluids - determination of the resistance to rapid crack propagation (RCP) - small scale steady state (S4)*: Draft International Standard DIS 13477, International Organization for Standardization, Geneva, Switzerland
- Anon. (1996) *Hoechst Product Literature for Hostalen® CRP 100* [available from: Hoechst Aktiengesellschaft, Hostalen PE Marketing, D-65926 Frankfurt am Main, Germany]
- Anon. (1996) *BP Product Literature on Rigidex® PC002-50*

- R102 for pipes [available from: BP Chemicals Ltd, Bo'ness Road, Grangemouth, UK FK3 9XH]
- 10 Anon. (1996) *Borealis Product Literature for HE2490 and HE2494* [available from: Lyngby Hovedgade 96, DK-2800, Denmark]
 - 11 Anon. (1995) *Solvay Product Literature on Eltex® TU B121, B124 and B125* [available from: Solvay S.A., Rue du Prince Albert 33, B-1050, Belgium]
 - 12 Scheirs, J. (1995) *ExcelPlas Report No. 5-95, Emerging processes and reactor configurations in polyolefin production* [available from: ExcelPlas Australia, PO Box 102, Moorabbin, 3189, Victoria, Australia]
 - 13 Scheirs, J. and Evers, G. (1996) in *The Polymeric Materials Encyclopedia* (Salamone, J., ed.), pp. 5965-5977, CRC Press
 - 14 Böhm, L.L., Bilda, D., Breuers, W., Enderle, H.F. and Lecht, R. (1995) in *Ziegler Catalysis* (Fink, C., Muhlhaupt, R. and Brintzinger, H.H., eds), pp. 387-400, Springer
 - 15 Böhm, L.L., Enderle, H.F. and Fleissner, M. (1994) in *Catalyst Design for Tailor-made Polyolefins* (Soga, K. and Terano, M., eds), pp. 351-363, Kodansha
 - 16 Scheirs, J. (1996) in *The Polymeric Materials Encyclopedia* (Salamone, J., ed.), pp. 5989-6001, CRC Press
 - 17 Pittman, J.F.T., Farah, I.A., Isaac, D.H. and Eccott, A. (1995) *Plast. Rubber Compos. Process. Appl.* 24, 123
 - 18 Böhm, L.L. (1981) *Makromol. Chem.* 182, 3291
 - 19 Lustiger, A. and Markham, R.L. (1983) *Polymer* 24, 1647
 - 20 Böhm, L.L., Enderle, H.F. and Fleissner, M. (1992) *Adv. Mater.* 4, 234
 - 21 Scholten, F.L. and Rijpkema, H.J.M. (1992) *Proc. Plastic Pipes VIII, Eindhoven, The Netherlands*, pp. C2/4-1-C2/4-10 [available from: Plastics and Rubber Institute, 11 Hobart Place, London, UK SW1W 0HL]
 - 22 Schouterden, P., Groenickx, G., Van der Heijden, B. and Jansen, F. (1987) *Polymer* 20, 2099
 - 23 Wild, L. (1990) *Adv. Polym. Sci.* 98, 1
 - 24 Holtrup, W. (1977) *Makromol. Chem.* 178, 2335
 - 25 Fuchs, O., Böhm, L., Fleissner, M., Gann, G., Suhr, H.H. and Schüddemage, H.D.R. (1971) in *Encyclopedia of Industrial Chemical Analysis* (Vol. 12) (Snell, F.D. and Ette, L.S., eds), p. 341, Interscience Publishers
 - 26 Scheirs, J. (1994) *ExcelPlas Report No. 18-94, Advanced methods for the characterization of commercial PE100 pipe resins* [available from: ExcelPlas Australia, PO Box 102, Moorabbin, 3189, Victoria, Australia]
 - 27 Gueugnaut, D. and Roussetot, D. (1995) *Proc. Plastic Pipes IX, Edinburgh*, p. 107 [available from: The Institute of Materials, Carlton House Terrace, London, UK SW1Y 5DB]
 - 28 Janson, L.E. and Molin, J. (1991) *Design and Installation of Buried Pipes*, Wavin Publishers
 - 29 Greig, J.M., Leevers, P.S. and Yaila, P. (1992) *Eng. Fract. Mater.* 42, 663
 - 30 UK Water Industry Engineering and Operations Committee (1993) *Specification for blue higher performance polyethylene, HPPE/PE100, pressure pipes nominal size 90 to 1000 mm, for underground or protected use for the conveyance of water intended for human consumption*, Water Industry Standard 4-32-13, WRC Publishers
 - 31 ISO (1993) *Methods of testing plastics. Part 3: Mechanical properties (methods 320A to 320F and 335A)*: ISO 178, International Organization for Standardization, Geneva, Switzerland
 - 32 Ifwarson, M. and Leijstrom, H. (1992) *Proc. Plastic Pipes VII, Eindhoven, The Netherlands*, paper No. C171 [available from: Plastics and Rubber Institute, 11 Hobart Place, London, UK SW1W 0HL]
 - 33 ISO (1995) *Polyolefin pipes for the conveyance of fluids - Resistance to crack propagation - Test method for slow crack growth of notched pipes*: ISO/DIS 13479, International Organization for Standardization, Geneva, Switzerland
 - 34 ASTM (1995) *Test method for notch tensile test to measure the resistance to slow crack growth of polyethylene pipes and resins (PENT Test)*: ASTM 1473 (Vol. 08.04), American Society for Testing Materials, Philadelphia, PA 19103, USA
 - 35 ISO (1993) *Polyethylene Plastic Pipes - determination of slow crack growth resistance (cone test method)*: ISO/DIS 13480, International Organization for Standardization, Geneva, Switzerland
 - 36 Beech, S.H., Channell, A.D. and Rose, L.J. (1995) *Proc. 14th Int. Plast. Fuel Gas Pipe Symp., San Diego*, pp. 216-225 [available from: the American Gas Association, Chicago, IL, USA]
 - 37 ISO (1995) *Thermoplastic pipes for the conveyance of fluids - determination of the resistance to rapid crack propagation (RCP) - full scale test (FST)*: Draft International Standard DIS 13478, International Organization for Standardization, Geneva, Switzerland
 - 38 Leevers, P.S., Venizelos, G.P. and Morgan, R.E. (1993) in *Buried Plastic Pipe Technology* (Vol. 2) [ASTM STP 1222] (Eckstein, D., ed.), pp. 133-148, American Society for Testing Materials, Philadelphia, PA 19103, USA
 - 39 Leevers, P.S. and Yaila, P. (1991) *Proc. 12th Plast. Fuel Gas Pipe Symp., Boston, Massachusetts, 24-26 September*, pp. 58-69 [available from: American Gas Association, Arlington, VA, USA]
 - 40 Wheel, M.A. and Leevers, P.S. (1993) *Int. J. Fracture* 61, 349
 - 41 Leevers, P.S. (1995) *Int. J. Fracture* 73, 109
 - 42 Clutton, E.Q. and Channell, A.D. (1995) in *Impact and Dynamic Fracture of Polymers and Composites* (ESIS Publication 19), pp. 215-224, Mechanical Engineering Publications
 - 43 Wilson, K.A. (1995) *Proc. Plastic Pipes IX, Edinburgh*, pp. 168-180 [available from: The Institute of Materials, Carlton House Terrace, London, UK SW1Y 5DB]
 - 44 Reade, L. (1996) *Eur. Plast. News* February, p. 24
 - 45 Anon. (1995) *Eur. Chem. News* 27 March, p. 6
 - 46 Anon. (1995) *Mod. Plast. Int.* September, p. 169

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